

Search and Characterization of Novel Superhard Phases in the B-C-N System Under Extreme Conditions

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The new diamond-like B-C phase was obtained from the graphite-like BC phase in a laser heated diamond anvil cell at high temperature, 2230 ± 140 K, and high pressure, 45 GPa. Raman spectra of the new phase measured at ambient conditions revealed a peak at 1315 cm^{-1} , which was attributed to longitudinal optical mode of a diamond-like B-C phase.

A bulk composite superhard material was synthesized from graphite-like BC_3 at 20 GPa and 2300 K using a multianvil press. The material consists of intergrown boron carbide B_4C and B-doped diamond with 1.8 at.%B. The material exhibits semiconducting behavior and extreme hardness comparable with that of single-crystal diamond.

Spectrochimica Acta Part A: Molec. Biol. Spectrosc., submitted in 2004.

Appl. Phys. Lett., **85**(8) 1-4 (2004).

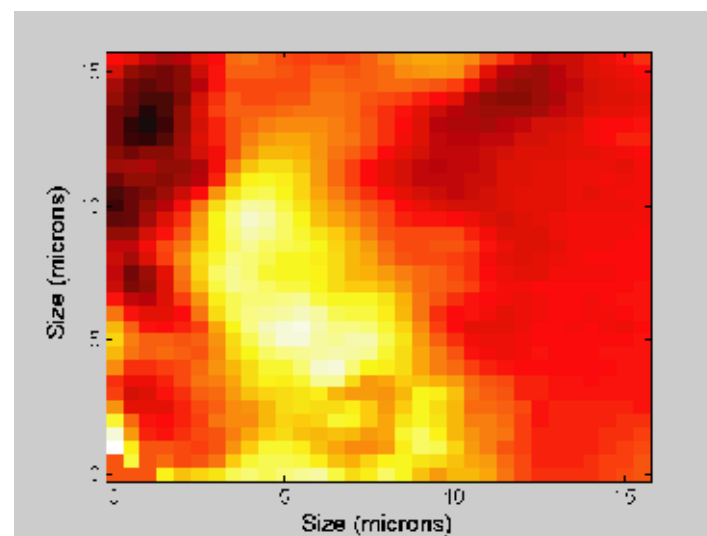


Fig. 1. Intensity XY mapping of peak 1315 cm^{-1} of the new diamond-like B-C phase .

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Novel high-pressure phase, cubic BC_x , ($8 \leq x \leq 10$), was synthesized at pressures 22-27 GPa and temperatures up to 2500 K by solid-state thermal decomposition of graphite-like BC using a laser-heated diamond anvil cell. The lattice parameter of the new phase at ambient conditions is 3.588(1) Å which is 0.6% larger than that of diamond. The effect of pressure on the volume of cubic BC_x up to 52 GPa is shown in the Fig. 2.

Using the two-parameter Birch Murnaghan equation of state to fit the data, we obtained values of bulk modulus $B_0 = 335(4)$ GPa and its pressure derivative $B_0' = 4.5(3)$. The bulk modulus (B_0) of cubic BC_x is smaller than those of diamond (442 GPa) and cBN (372 GPa), however, this phase still has one of the largest bulk moduli known for any solid.

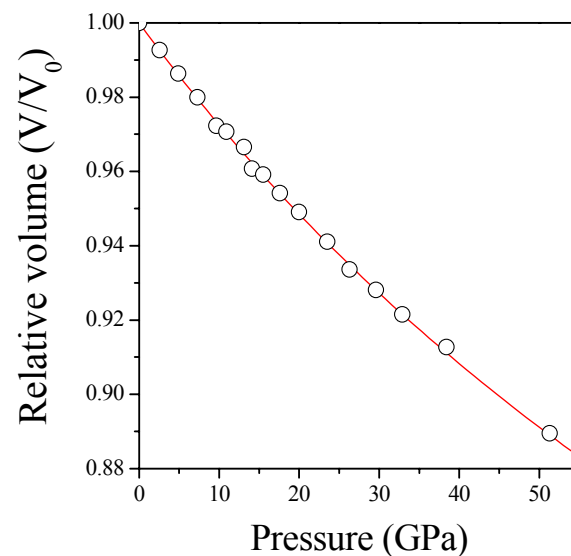


Fig. 2. The effect of pressure on the volume of BC_x to 52 GPa at room temperature

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Liu and Cohen in 1989 first predicted theoretically that some denser forms of C_3N_4 such as the β - C_3N_4 phase should exhibit a bulk modulus and hardness higher than those of diamond because of the short length and high covalence of the C-N bond. Since then there has been much interest in studying the C-N system at high pressures and temperatures. In our recent study, we have subjected a turbostratic carbon nitride (t-CN) to 22 GPa (i.e., 2.2×10^5 atmospheres) and to 2250 K in a large-volume press. The fact that no β - C_3N_4 phase was obtained in this study suggests either the synthesis pressure is too low or the denser phase may only occur under a high nitrogen pressure so as to prevent the decomposition of the C_3N_4 .

Indeed, Raman measurements of the phase obtained from turbostratic carbon nitride at high pressure (>40 GPa) and high temperature (2000K). Fig 3 is an image showing the difference between the heated and the unheated area of the sample in a diamond-anvil cell. Identification of the new phase using x-ray diffraction is now in progress.

J. Phys. Chem. Sol. 64(8) 1265-1270 (2003).

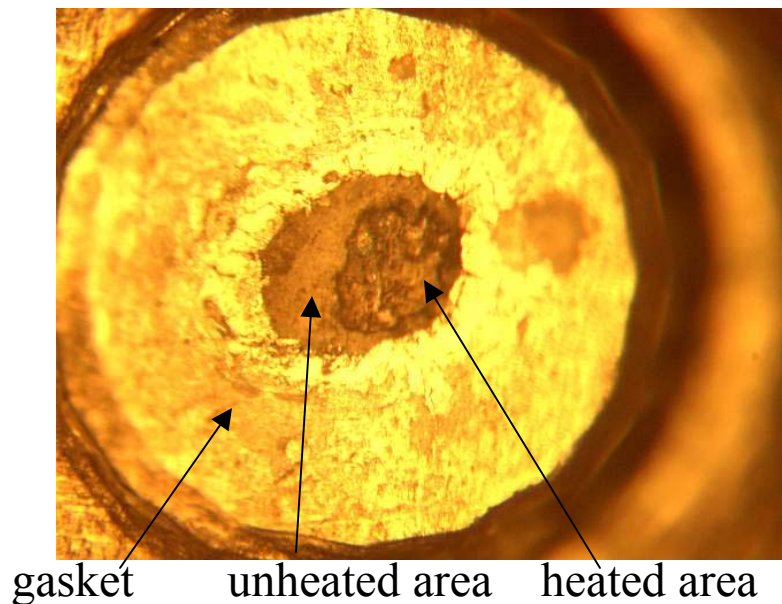


Fig. 3. An optical image of the turbostratic carbon nitride (t-CN) heated by a CW YAG laser in a diamond-anvil cell.

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Superhard diamond-like ternary B-C-N phases are highly desirable, as they might combine the best properties of the elemental or binary compounds of the system. For example, a diamond-cBN alloy should be more thermally stable and resistant to oxidation, less reactive with iron than pure diamond, and harder than cBN. Here we present AFM image showing the nanostructure of the new BC_2N phase obtained under high pressure and high temperature (Figure 4).

The first Brillouin scattering measurements on nanocrystalline cubic phase of BC_2N have been successfully performed using the “modified” platelet scattering geometry (Fig.5). We were able to measure both longitudinal (V_p) and shear (V_s) velocities independent of refractive index, and thus obtained values of 13.09 ± 0.22 km/s and 8.41 ± 0.14 km/s, respectively. Our results indicate the new nanocrystalline cubic BC_2N phase is a new material with intriguing physical properties – while its hardness is higher than that of cBN, its velocities, and thus the bulk and shear moduli are all smaller than those of cBN.

1. *Phys. Rev. B* **68**(5) 052104(3) (2003).
2. *Ultrasonic Nondestructive Evaluation*, T. Kundu ed., CRC Press, Boca Raton, 581-651 (2004).
3. *J. Mater. Sci.Lett.* submitted (2004.)

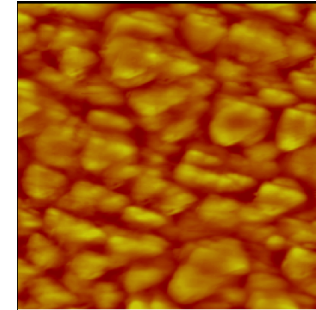


Fig. 4. Nanostructure of cubic BC_2N nanophase of 200 nm obtained by AFM image (tapping mode, scale $2 \times 2 \mu m$).

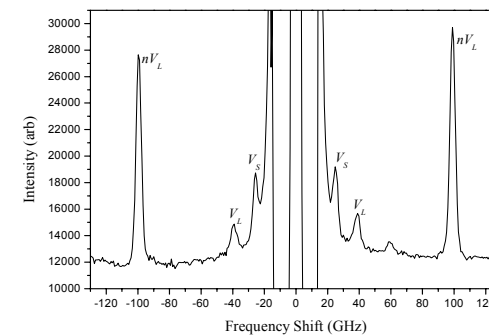


Fig. 5. Experimental BS spectrum ($\theta = 50^\circ$) of nanocrystalline $c\text{-}BC_2N$.

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Raman measurements were conducted with the nanocrystalline cubic BC_2N sample and gave us a mean Raman shift of 1325.7 cm^{-1} (see Fig. 6). This position of the Raman band is located between the Raman peak of diamond (1332 cm^{-1}) and that of cubic $\text{C}_{0.3}(\text{BN})_{0.7}$ (1323 cm^{-1}), showing the Raman shift decreases with decreasing the number of C atoms and is positively deviated from the straight line between the two end members (diamond and cBN at 1304 cm^{-1}). The large width of the observed 1325.7 cm^{-1} most likely reflects random substitution of B and N atoms in the diamond lattice, which is also consistent with the cubic- BC_2N being disorder as revealed from the synchrotron-based x-ray diffraction data.

J. Raman Spectr., in press (2004).

Education:

Two graduate students (Sergey Tkachev, and Alexander Kurakevich) and a post-doctoral associate (Dr. V.L. Solozhenko) have made contributions to this work.

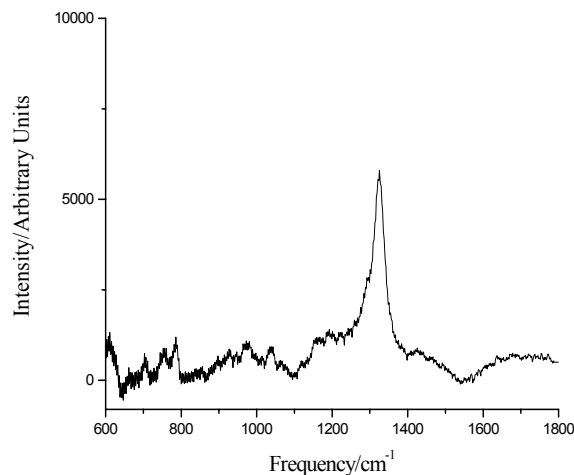


Fig. 6. Raman spectrum of the BC_2N phase measured by UV laser .